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Substituent and solvent effects on intramolecular charge transfer of 5-arylidene-2,4-thiazolidinediones

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1. Introduction

2,4-Thiazolidinedione (TZD) is an interesting structural unit in medicinal chemistry and responsible for numerous pharmacological properties and biological activities, *e.g.*, antidiabetic [1], antiarthritic [2], antibacterial [3] and oncostatic [4]. Due to this, structures and relative stabilities of the potential tautomeric forms of TZD derivatives have been extensively studied from both theoretical and experimental point of view [5–7]. Electronic spectra of these molecules have been investigated mostly for reasons of the determination of their acidities and basicities, as well as the energies of protonation and deprotonation [8,9]. An *ab initio* HF and MP2 study of static hyperpolarizability of TZD has also been reported [10].

The second-order nonlinear optical properties arise from a non-centrosymmetric π -conjugated charge-transfer (CT) molecule containing both electron donor and electron acceptor groups connected by an electron-transmitting bridge. The importance of heterocycles in the design of such donor–acceptor systems has been extensively discussed [11–13]. 5-Arylidene-2,4-thiazolidinediones are expected to be useful as second-order nonlinear optical materials from the electron deficient TZD moiety and the arylidene part of molecule designed to be responsive to the TZD demand, respectively. While 5-arylidene-2,4-thiazolidinedione takes a

ABSTRACT

The absorption spectra of twelve 5-arylidene-2,4-thiazolidinediones were recorded in twenty one solvents in the range from 300 to 600 nm. The effect of specific and non-specific solvent–solute interactions on the absorption maxima shifts were evaluated by using the Catalán solvent parameter set. Furthermore, the experimental findings were interpreted with the aid of *ab initio* MP2 and time-dependent density functional (TD-DFT) methods. It was found that different substituents significantly change the extent of conjugation in the molecules and further affect their intramolecular charge transfer character.

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centrosymmetric molecular arrangement in crystalline state, the introduction of a methoxy group into *para*-position of phenyl moiety causes enhancement of molecular hyperpolarizability (β) and brings about a non-centrosymmetric molecular arrangement [14]. It has been established that the photophysical properties of these derivatives are mainly governed by the polarity of the medium, hydrogen bonding and electronic substituent effects at arylidene moiety [15]. The absorbance and the fluorescence spectra reflect their solvent polarity dependence, whereas the diminished fluorescence intensities in polar solvents indicate the formation of hydrogen bonds resulting in radiationless decay.

In this work, twelve 5-arylidene-2,4-thiazolidinediones (Fig. 1a) were synthesized in order to characterize their absorption bands, as well as to study contributions of appropriate substituent- and solvent-dependent electronic transitions observed in the corresponding spectra. The absorption spectra were recorded in the range from 300 to 600 nm in 21 solvents of different properties. The influence of the interactions of these molecules with the surrounding media was investigated by solvatochromic studies, whereby the appropriate contributions of the specific solvent-solute interactions can be defined (Fig. 1a). The effects of solvent dipolarity, polarizability and solvent-solute hydrogen bonding interactions were evaluated by means of the linear solvation energy relationship (LSER) model of Catalán [16], given by Eq. (1):

$$\nu = \nu_0 + aSA + bSB + cSP + dSdP \tag{1}$$

where SA, SB, SP and SdP characterize solvent acidity, basicity, polarizability and dipolarity of a solvent, respectively; and a-d

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Fig. 1. Structures of the investigated 5-arylidene-2,4-thiazolidinediones, where X is: H (1); Me (2); iPr (3); OMe (4); OEt (5); OH (6); NH₂ (7); NMe₂ (8); Cl (9); Br (10); CN (11) and NO₂ (12) with possible solvent–solute interaction modes (a), and the optimized conformation of 5-benzylidene-2,4-thiazolidinedione (b).

are the regression coefficients describing the sensitivity of the absorption maxima to the different types of the solvent–solute interactions. The advantage of this concept is that it gives possibility to separate non-specific solvent effects into two terms: dipolarity and polarizability.

Additionally, the linear free energy relationship (LFER) methodology was applied to the v_{max} of the studied TZD derivatives with the aim to get an insight into factors determining the absorption maxima shifts. The transmission of electronic substituent effects (Fig. 1a) was studied using the simple Hammett equation:

$$s = \rho \sigma + h \tag{2}$$

where *s* is a substituent-dependent value: absorption frequencies (v_{max}) , ρ is the proportionality constant reflecting the sensitivity of the v_{max} to the substituent effects, σ is the corresponding substituent constant, and *h* is the intercept (*i.e.*, describes the unsubstituted member of the series) [17]. Eq. (2) attributes the observed substituent effect to an additive blend of polar and π -delocalization effects given as corresponding σ values.

Ab initio MP2 calculations indicate non-planar conformations of the investigated TZD derivatives. The contributions of electronic substituent effects were further discussed in relation to the geometry found by MP2 calculations. The most stable conformation of 5-benzylidene-2,4-thiazolidinedione is presented by the structure in Fig. 1b. Time-dependent density functional theory (TD-DFT) appears to be quite successful for the states of solvated organic molecules corresponding to an electronic transfer from a donor group to an acceptor moiety [18] or to twisted intramolecular charge transfer (ICT) situations [19]. With the help of a TD-DFT model systematically accounting for solvent effects, the absorption spectra were computed in order to obtain the best similarity to experimental ones.

2. Experimental

5-Arylidene-2,4-thiazolidinediones were synthesized by Knoevenagel condensation of 2,4-thiazolidinedione (TZD) with appropriate aryl aldehydes [20].The UV absorption spectra were measured with a Shimadzu 1700 UV/vis spectrophotometer. The UV/vis spectra were taken in spectro quality solvents (Fluka) at a concentration of 1×10^{-5} mol dm⁻³ and showed no dependence on the concentration.

Geometries of all twelve molecules were fully optimized with MP2/6-31G(**) method. Global minima were found for every molecule. Theoretical absorption spectra were calculated in gas phase and ethanol solution with TD-DFT method for molecules **1**, **8** and **12** on optimized geometry with B3LYP functional and 6-31G(**) basis set. Solvent was simulated with static isodensity

surface polarized continuum model (IPCM). All calculations were done with Gaussian03 software [21].

The correlation analysis was carried out using Microsoft Excel software that considers the 95% confidence level. The goodness of fit is discussed using the correlation coefficient (R), the standard error of the estimate (sd), and Fisher's significance test (F).

3. Results and discussion

A generally accepted concept, for the relationship between molecular structure and absorption spectrum, requires the maximum planarity to produce red shift due to the increase of π -conjugation. Based on this, a series of TZDs coupled with *para*-substituted benzaldehydes was synthesized, supposing that the obtained π -conjugated systems show different sensitivities towards solvent and substituent effects.

The absorption spectra of the investigated compounds were recorded in 21 solvents in the range from 300 to 600 nm and the characteristic cases in representative solvents are shown in Fig. 2. It can be seen that some absorption bands (*e.g.*, **3**, **9**, **10**, **11**) are broadened and split in the protic solvent ethanol. This splitting is proposed to originate from the keto-enol tautomerization. The main absorption is assigned to ICT transition in the keto form and the corresponding maxima are collected in Table 1. The low-energy shoulder appearing mostly in protic solvents arises from the enol form. However, the further discussion is directed only to absorption maxima of the keto form of the investigated compounds due to the higher stability and presence in all used solvents.

The absorption maxima of all compounds showed red shift relative to **1** and were also red-shifted with increasing solvent polarity and hydrogen-bonding capacity. Thus, the introduction of electron donor substituents into the arylidene part produces larger red shifts compared to electron acceptors suggesting a more pronounced CT interaction in a molecule.

3.1. Solvent effects

The effect of various types of solvent–solute interactions on the absorption maxima shifts was interpreted by means of the linear solvation energy relationship (LSER) model of Catalán. The Catalán parameters for the solvents used in correlations are listed in Table 2. The regression values v_0 , *a*, *b*, *c* and *d* fit at the 95% confidence level are presented in Table 3.

The success degree of the quantification and interpretation of solvent effects on the absorption frequencies of the investigated molecules is shown in Fig. 3 by means of a plot of ν observed (ν_{exp}) versus ν calculated (ν_{calc}) in different solvents (R = 0.997, sd = 0.16, F = 33,627).

Table 1

The absorption frequencies of the investigated compounds in selected solvents.

Solvent/No.	$v_{max} \times 10$	$^{-3}$ (cm ⁻¹)										
	1	2	3	4	5	6	7	8	9	10	11	12
Water	30.26 ^b	29.72 ^b	29.59 ^b	28.78	28.61	28.61	26.54	23.87	29.85 ^b	29.72 ^b	30.53 ^a	29.28
Methanol	31.06	30.49	30.40	29.03	28.94	28.78	25.67	24.48	30.72	30.44	30.30	29.07
Ethanol	30.96	30.40	30.35	29.15	29.11	28.74	25.51	24.63	30.63	30.40	30.35	28.82
2-Propanol	30.91	30.49	30.26	29.24	28.94	28.45	25.54	24.75	30.53	30.35	30.35	29.07
1-Butanol	30.92	30.28	30.30	29.15	28.92	28.56	25.59	24.63	30.43	30.30	30.12	28.84
2-Methyl-2-propanol	30.86	30.35	30.21	29.15	28.90	28.25	25.32	24.60	30.58	30.40	30.35	29.15
1-Hexanol	30.90	30.40	30.32	28.97	28.99	28.51	25.38	24.61	30.54	30.40	30.23	28.89
Ethylene glycol	30.56	29.87	29.83	28.67 ^b	28.56	28.28	25.35	23.78 ^b	30.16	29.90	29.24	28.28
Tetrahydrofuran	31.00	30.47	30.41	29.19	29.10	28.95	25.93	24.83	30.60	30.47	30.34	28.94
Disopropyl ether	31.11 ^a	30.62 ^a	30.58 ^a	29.48	29.38	29.14	26.50	25.23	30.73 ^a	30.66 ^a	30.49	29.36
Dimethyl sulfoxide	30.60	30.05	29.92	28.67 ^b	28.54	28.17	24.83 ^b	23.99	30.19	29.82	28.80	27.46
Methyl acetate	31.09	30.51	30.41	29.22	29.14	29.22 ^a	26.33	24.76	30.67	30.60	30.49	29.24
Ethyl acetate	31.04	30.54	30.38	29.31	29.24	28.99	26.22	24.93	30.67	30.66 ^a	30.41	29.21
N,N-Dimethylformamide	30.41	30.32	30.23	29.64 ^a	29.64 ^a	28.82	26.88ª	26.55ª	30.19	29.94	28.70	26.25
N,N-Dimethylacetamide	30.60	30.28	30.14	28.95	28.87	28.60	25.13	24.37	30.08	29.98	28.60 ^b	25.76
Chloroform	30.75	30.01	29.98	28.84	28.65	28.30	25.69	24.06	30.40	30.21	30.05	28.80
Anisole	30.54	29.92	29.83	28.70	28.59	28.90	26.25	24.21	30.03	29.98	29.94	28.74
Acetic acid	30.86	30.17	30.08	28.69	28.49 ^b	28.53	26.14	24.10	30.40	30.40	30.35	29.11
Acetonitrile	31.06	30.44	30.30	29.24	28.94	29.15	26.46	24.51	30.63	30.53	30.40	29.15
Pyridine	30.56	30.01	29.96	28.87	28.64	28.14 ^b	25.47	24.37	30.16	30.07	28.60 ^b	28.36
Heptane	31.10	30.53	30.40	29.37	29.24	29.03	26.32	24.91	30.63	30.53	30.53 ^a	29.28
$\Delta \nu (\mathrm{cm}^{-1})$	850	900	990	970	1150	1080	2050	2770	880	940	1930	3600

^a Solvent with the highest hypsochromic shift.

^b Solvent with the highest bathochromic shift.



Fig. 2. The absorption spectra of 5-arylidene-2,4-thiazolidinediones in ethanol (a) and anisole (b).



Fig. 3. The plot of v_{exp} against v_{calc} .

The correlation results obtained according to Eq. (1) (Table 3) imply that the solvent polarizability is the principal factor influencing the shift of v_{max} , whereas the solvent dipolarity, acidity and basicity have moderate to low contribution to solvatochromic properties of the investigated compounds. Negative values of the coefficients *c* and *d* indicate higher solvent dipolarity and polarizability effects in the electronic excited state compared with the ground state. Therefore, the neutral resonance structure (Figs. 4 and 5; structure I) clearly dominates over the zwitterionic ones (Fig. 4; structures II–IV and Fig. 5; structures V and VI) in the ground state, whereas in the excited state the reverse situation is found. This behavior is in fact typical for ICT processes.

A low variation in the *c* values is observed for the electron donor substituted derivatives (2-8), indicating a lower contribution of extended resonance transmission. Obviously, the UV/vis absorption of these compounds is more substituent-dependent than solvent-dependent (Table 1). Although the TZD moiety acts as an electron acceptor group, the introduction of different electron

Table 2Solvent parameters [16].

Solvent	SP	SdP	SA	SB
Water	0.681	0.997	1.062	0.025
Methanol	0.608	0.904	0.605	0.545
Ethanol	0.633	0.783	0.400	0.658
2-Propanol	0.633	0.808	0.283	0.830
1-Butanol	0.674	0.655	0.341	0.809
2-Methyl-2-propanol	0.632	0.732	0.145	0.928
1-Hexanol	0.698	0.552	0.315	0.879
Ethylene glycol	0.777	0.910	0.717	0.534
Tetrahydrofuran	0.714	0.634	0.000	0.591
Disopropyl ether	0.645	0.286	0.000	0.666
Dimethyl sulfoxide	0.830	1.000	0.072	0.647
Methyl acetate	0.645	0.637	0.000	0.527
Ethyl acetate	0.656	0.603	0.000	0.542
N,N-Dimethylformamide	0.759	0.977	0.031	0.613
N,N-Dimethylacetamide	0.763	0.987	0.028	0.65
Chloroform	0.783	0.614	0.047	0.071
Anisole	0.820	0.543	0.084	0.299
Acetic acid	0.651	0.676	0.689	0.390
Acetonitrile	0.645	0.974	0.044	0.286
Pyridine	0.842	0.761	0.033	0.581
Heptane	0.635	0.000	0.000	0.083

donor substituents does not significantly influence the variation in the mobility of the π -electrons, *i.e.*, enhance the molecule polarizability. It is expected that the highly π -conjugated structures have the highest polarizability. A greater extent of resonance interaction is operative within more planar π_1 - and π_2 -resonance units (Fig. 4; structure IV) causing larger localized π -electronic density shifts. The largest red shifts of compounds **7** and **8** are consistent with the strongest electron-donating properties of the NMe₂ and NH₂ groups.

The opposite is observed for the electron acceptor substituted derivatives (**9–12**). The molecular polarizability is also conformation-dependent property and could be to an appropriate extent a consequence of the transmission of electronic substituent effects. The large polarizability of these compounds indicates that the π -electronic polarization is not necessarily transmitted through the whole π -network, but the polarization of each localized π -unit is of higher significance. This is ascribed to the destabilization of the TZD moiety by electron acceptor groups causing the change in the electronic distribution to be more sensitive to solvent effects.

Dipolar solvent–solute interactions, assigned with the *d* term, are of importance only if a strong electron donor (except compound **6**) or acceptor substituent is present in the arylidene part of the molecule. However, the electron donors influence dipolar characteristics of the investigated molecules differently from the electron acceptors. Electronic substituent effects, polar (field/inductive) and resonance, transmitted through the molecule, cause the separation of charges susceptible to solvent dipolar interactions. It seems that the higher contribution of the solvent dipolar effect towards the electron acceptor substituted derivatives **11** and **12** is due to two distinct π -electronic entities: the arylidene and TZD moieties that possess dipolar characteristic differently oriented in space. It is typical for styrene derivatives that the zwitterionic state of the derivatives with an electron acceptor substituent has a much larger



Fig. 4. Resonance structures of electron donor substituted 5-arylidene-2,4-thiazolidinediones.



Fig. 5. Resonance structures of electron acceptor substituted 5-arylidene-2,4-thiazolidinediones.

Table 3		
Regression fits to the	solvatochromic	parameters.

No.	$ u_o \times 10^{-3} $ (cm ⁻¹)	$a \times 10^{-3}$ (cm ⁻¹)	$b \times 10^{-3}$ (cm ⁻¹)	$c \times 10^{-3}$ (cm ⁻¹)	$d imes 10^{-3}$ (cm ⁻¹)	R ^a	sd ^b	F ^c	Solvents excluded from the correlation ^e
1	32.64 (±0.18)	-0.24 (±0.08)	_d	-2.47 (±0.25)	-	0.928	0.08	49.4	W, DMF
2	32.15 (±0.21)	-0.51 (±0.07)	0.21 (±0.08)	-2.65 (±0.27)	-	0.948	0.09	50.3	-
3	31.89 (±0.26)	$-0.49 \ (\pm 0.08)$	0.22 (±0.10)	$-2.44 (\pm 0.34)$	-	0.914	0.11	28.6	-
4	31.06 (±0.22)	-0.38 (±0.08)	-	$-2.60 \ (\pm 0.28)$	$-0.14 \ (\pm 0.09)$	0.949	0.08	45.5	DMF, AcOH
5	30.85 (±0.22)	-0.30 (±0.09)	0.18 (±0.09)	$-2.50 \ (\pm 0.32)$	-0.28 (±0.11)	0.952	0.09	31.1	tBuOH, DMF, AcOH
6	31.83 (±0.39)	-0.66 (±0.13)	-0.93 (±0.18)	-3.02 (±0.50)	$-0.43 \ (\pm 0.20)$	0.930	0.14	19.2	tBuOH, DMF, Chl, Hp
7	30.28 (±0.34)	-0.33 (±0.12)	-2.13 (±0.15)	$-3.16 (\pm 0.44)$	-1.31 (±0.18)	0.977	0.13	68.6	DMF, Chl, Hp
8	26.78 (±0.36)	-0.62 (±0.14)	0.38 (±0.14)	$^{-2.88}_{(\pm 0.50)}$	-0.48 (±0.17)	0.939	0.15	28.0	DMF
9	32.25 (±0.26)	$-0.44 \ (\pm 0.09)$	0.20 (±0.10)	$^{-2.63}_{(\pm 0.34)}$	-	0.930	0.11	29.7	MeOH, DMAc, Chl
10	32.80 (±0.25)	-0.39 (±0.09)	-	-2.93 (± 0.36)	$-0.50 \ (\pm 0.14)$	0.938	0.11	38.9	Нр
11	36.82 (±0.71)	-	-1.02 (±0.28)	$^{-7.44}_{(\pm 0.91)}$	-1.44 (±0.35)	0.927	0.29	32.3	Нр
12	40.36 (±1.79)	1.16 (±0.46)	-1.69 (±0.53)	-10.93 (±2.10)	-4.60 (± 0.82)	0.918	0.48	14.7	iPr ₂ O, DMSO, AcOH, Py, Hp

^a Correlation coefficient.

^b Standard deviation.

^c Fisher test of significance.

^d Negligible values with high standard errors.

^e Abbreviations taken from www.chemnetbase.com.

dipole moment than those of the parent molecule and derivatives with an electron donor substituent [22]. The better stabilization of the excited state relative to the ground state in dipolar solvents results in red shift and depends mainly on the solute dipole moment change during the transition.

Specific solvent-solute interactions through hydrogen bonding, i.e., solvent acidity and basicity, can be attributed mainly to the carbonyl and NH groups of the TZD moiety. Low negative values of the coefficient *a* for compounds 1-10 indicate moderate to low contribution of the solvent acidity to the stabilization of the excited state of the investigated compounds. It might be a consequence of the long-range transmission of substituent effects, which supports the larger polarization of both carbonyl groups and, in that way, enhances the hydrogen bonding capabilities of carbonyl oxygens. The highest contribution of the solvent acidity to solvatochromic properties was observed for compounds 6 and 8. Such observation indicates that the overall hydrogen-bond accepting ability of these compounds originate from the appropriate contributions of the substituent lone pair and the TZD moiety proton-accepting sites. These observations indicate that solvent achieves the higher extent of hydrogen bonding with nucleophilic sites at the TZD moiety, and its low dependence on substituent effects was observed (Table 3). Moreover, solvent-dependent hypsochromic shifts of $v_{\rm max}$ observed for compound 12 indicates that this molecule is more susceptible to the solvent HBD stabilization in the ground state, due to a higher contribution of the structures II and III (Fig. 4). Basically, deviation from the general trend of the value of the coefficient *a* for compound **12** (Table 3) is a consequence of the appropriate geometry and transmission mode of substituent effects.

The highest contribution of the solvent HBA effect was observed for compound **12**, while it was lower for **6**, **7** and **11**, in line with

the stabilization of the solute in the excited state. High values of the coefficient *b* for electron acceptor substituted compounds **11** and **12** are a consequence of the strong electron-accepting properties of NO₂ and CN groups, and the contribution of the both carbonyl groups polarization (Fig. 4; structures II and III) contributing an increased NH proton-donating ability. Although substituents with +M effect (compound **6** and **7**) cause an increase of the electron density at the TZD moiety, their proton-donating capability is significant, regardless if it comes from substituent or the TZD moiety. Positive sign and lower values of the coefficient *b* for other compounds (Table 3), considering the electron donor substitued compounds, clearly indicate the significance of proton-donating capabilities of OH and NH₂ substituents.

3.2. Substituent effects

In an attempt to assess substituent effects on ICT of the investigated molecules, the principles of liner free energy relationships (LFER) were applied to the UV/vis spectral data using Eq. (2). The correlation results are given in Table 4.

The correlation results (Table 4), obtained separately for the electron donor and electron acceptor substituted derivatives, reflect different transmission modes of electronic substituent effects through differently oriented π -electronic units (Fig. 1a). The introduction of an electron donor substituent enhances the positive solvatochromism of the molecules and also results in a higher susceptibility of the absorption maxima shifts to electronic substituent effects. Concerning the electron acceptor substituted derivatives, a significantly lower sensitivity is observed. Higher sensitivities of their absorption frequencies to substituent effects in a protic dipolar solvents (DMSO, DMF and DMAc) can be explained by the fact that,

Table 4

Regression fits according to Eq. (2) for the electron donor and acceptor substituted derivatives.

Solvent	Electron-dono	or substituted deri	vatives (1-8)			Electron-acceptor substituted derivatives (1, 9-12)				
	$ u_0 \times 10^{-3} $ (cm ⁻¹)	$ ho imes 10^{-3}$ (cm ⁻¹)	R	sd	F	$ \frac{\nu_o \times 10^{-3}}{(cm^{-1})} $	$ ho imes 10^{-3}$ (cm ⁻¹)	R	sd	F
Water	30.71 (±0.32)	7.32 (±0.74)	0.970	0.54	97	30.14 (±0.10)	-1.16 (±0.25)	0.957	0.14	22
Methanol	31.42 (±0.23)	8.38 (±0.54)	0.988	0.39	245	31.13 (±0.12)	-2.60 (±0.27)	0.989	0.16	90
Ethanol	30.39 (±0.22)	8.29 (±0.51)	0.989	0.37	263	31.08 (±0.13)	-2.83 (±0.30)	0.989	0.17	91
2-Propanol	31.30 (±0.23)	8.00 (±0.53)	0.987	0.39	232	30.96 (±0.08)	-2.39 (±0.18)	0.994	0.10	180
1-Butanol	31.28 (±0.20)	8.13 (±0.47)	0.990	0.34	304	30.96 (±0.06)	-2.69 (±0.13)	0.998	0.08	413
2-Methyl-2-propanol	31.24 (±0.22)	8.29 (±0.52)	0.988	0.38	255	30.95 (±0.09)	-2.26 (±0.22)	0.990	0.13	102
1-Hexanol	31.30 (±0.23)	8.30 (±0.53)	0.988	0.39	243	31.01 (±0.10)	-2.66 (±0.23)	0.993	0.13	136
Ethylene glycol	30.95 (±0.19)	8.43 (±0.45)	0.991	0.33	346	30.65 (±0.12)	-2.99 (±0.28)	0.991	0.16	113
Tetrahydrofuran	31.39 (±0.17)	7.90 (±0.51)	0.988	0.37	244	31.09 (±0.19)	-2.71 (±0.20)	0.994	0.12	178
Disopropyl ether	31.18 (±0.19)	7.44 (±0.44)	0.990	0.32	288	29.96 (±0.06)	-2.29 (±0.13)	0.997	0.08	292
Dimethyl sulfoxide	31.01 (±0.24)	8.67 (±0.56)	0.988	0.41	241	30.82 (±0.21)	-4.19 (±0.51)	0.987	0.29	68
Methyl acetate	31.45 (±0.23)	7.79 (±0.55)	0.985	0.40	200	31.15 (±0.05)	-2.42 (±0.12)	0.997	0.07	385
Ethyl acetate	31.42 (±0.19)	7.71 (±0.45)	0.990	0.33	294	31.15 (±0.08)	-2.43 (±0.19)	0.994	0.11	155
N,N-Dimethyl formamide	30.25 (±0.20)	5.44 (±0.45)	0.980	0.33	149	29.96 (±0.19)	-5.76 (±1.07)	0.967	0.61	29
N,N-Dimethyl acetamide	31.18 (±0.27)	8.35 (±0.64)	0.983	0.47	172	31.16 (±0.43)	-6.62 (±1.02)	0.977	0.58	42
Chloroform	31.05 (±0.17)	8.22 (±0.41)	0.993	0.30	401	30.83 (±0.10)	-2.56 (±0.23)	0.992	0.13	129
Anisole	30.88 (±0.28)	7.47 (±0.66)	0.977	0.49	127	30.54 (±0.02)	-2.31 (±0.04)	1.000	0.03	2769
Acetic acid	31.07 (±0.26)	8.00 (±0.61)	0.983	0.45	174	30.90 (±0.03)	-2.27 (±0.07)	0.999	0.04	1175
Acetonitrile	31.40 (±0.26)	7.83 (±0.61)	0.982	0.45	162	31.11 (±0.06)	-2.49 (±0.13)	0.997	0.08	359
Pyridine	30.93 (±0.18)	7.95 (±0.43)	0.991	0.32	343	30.69 (±0.11)	-2.92 (±0.25)	0.993	0.15	133
Heptane	31.46 (±0.19)	7.71 (±0.44)	0.990	0.32	308	31.11 (±0.04)	-2.34 (±0.09)	0.999	0.05	688

at high relative permittivity of surrounding medium, the energy necessary to bring about charge separation in the excited state is relatively small, which gives rise to a higher susceptibility to electronic substituent effects.

In addition, the geometries of the investigated molecules were fully optimized by the use of *ab initio* MP2 method. The significant stability of the diketo tautomer was obtained and results of geometry calculation are presented in Table 5.

It can be seen that the geometric features of the substituted derivatives are very similar to those of the unsubstituted one. However, the relationship between structure and the main absorption band is not fully consistent with the above-mentioned concept. The main absorption bands of the electron-donor substituted derivatives (2-8) appear at longer wavelengths ($\sim 20-100$ nm) compared

to those of **1**. An electron donor substituent supports an electron density shift from the π_1 -unit to the TZD moiety causing whole molecule planarization. A decrease in the C4–C5 bond length, which is a part of the enone system (π_2 -unit), indicates a greater extent of the π , π -delocalization. Thus, the carbonyl groups are slightly longer in the electron donor substituted derivatives. This result is an additional support for the extended conjugation operative in the π_1 - and π_2 -unit, *i.e.*, the π -electron density shifts towards C4=O carbonyl group increasing both carbonyl bond lengths and supporting *n*, π -conjugation in the π_3 -unit.

The results are quite the opposite for the electron acceptor substituted compounds (**9–12**). The deviation from the planarity increases with increasing electron acceptor ability of the arylidene substituent. An increase in the C4–C5 bond length indicates that

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Table	5

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No.	Interatomic o	Interatomic distance (Å)										
	C2-N3	N3-C4	C4-C5	C5-C6	C6-C7	C4=0	C2=0	θ(°)				
1	1.3867	1.3909	1.4925	1.3505	1.4573	1.2224	1.2138	27.36				
2	1.3867	1.3912	1.4919	1.3507	1.4560	1.2225	1.2140	26.60				
3	1.3866	1.3913	1.4918	1.3508	1.4558	1.2225	1.2140	26.42				
4	1.3862	1.3918	1.4904	1.3513	1.4536	1.2229	1.2142	23.89				
5	1.3862	1.3919	1.4903	1.3513	1.4534	1.2229	1.2143	23.79				
6	1.3863	1.3916	1.4908	1.3511	1.4542	1.2228	1.2141	24.52				
7	1.3857	1.3926	1.4891	1.3517	1.4521	1.2230	1.2145	22.52				
8	1.3855	1.3931	1.4882	1.3524	1.4501	1.2233	1.2148	20.99				
9	1.3866	1.3906	1.4931	1.3510	1.4557	1.2222	1.2133	25.96				
10	1.3866	1.3905	1.4933	1.3510	1.4558	1.2222	1.2133	26.04				
11	1.3867	1.3898	1.4949	1.3515	1.4560	1.2220	1.2127	26.57				
12	1.3867	1.3897	1.4949	1.3519	1.4558	1.2221	1.2126	26.53				

Table 6

Calculated energies of the HOMO and LUMO orbitals and energy gap for compounds 1, 8 and 12 in gas phase and ethanol.

No.	Gas phase			Ethanol	Ethanol			
	E _{HOMO} (eV)	E_{LUMO} (eV)	$E_{\rm gap}~({\rm eV})$	E _{HOMO} (eV)	E_{LUMO} (eV)	$E_{\rm gap}~({\rm eV})$		
1	-6.37	-2.26	4.11	-6.25	-2.18	4.07		
8	-5.46	-1.89	3.57	-5.37	-1.96	3.41		
12	-6.94	-3.56	3.72	-6.20	-3.05	3.16		

two opposite electron accepting effects operate in the π_2 -unit: electron accepting arylidene group and TZD carbonyl groups causing a non-planar geometrical adjustment together with low sulfur positive resonance participation as a response to electronic demand of the electron deficient environment (Fig. 5; structure VI). The normal carbonyl groups polarization is suppressed and causes a slight bond length decrease. Nevertheless, the longer λ_{max} are obtained than for **1**.

Mechanism of electronic excitations and changes in the overall charge distribution in both ground and excited states of the investigated molecules were studied by calculation of the energy gaps between the HOMO and LUMO orbitals for the unsubstituted derivative (1) and derivatives having a strong electron donor (8) and a strong electron acceptor substituent (12) in the arylidene part, and results are presented in Fig. 6 and Table 6.

Compound **1** has the largest energy gap with 4.11 eV, while somewhat smaller energy gaps for compounds **8** and **12** with 3.56 and 3.72 eV, respectively, were observed. This is consistent with red shift of their absorption maxima relative to those of **1**. Inclusion of solvent effects through TD-DFT calculations leads to a decrease in energy gaps by 0.08–0.56 (Table 6). Furthermore, the ICT character can be clearly observed during the orbital transition process from the HOMO to LUMO. It can be noticed that the electron densities of the HOMO and LUMO orbitals for **8** are separately populated on the phenyl ring and the TZD moiety, respectively, confirming its strong ICT character. The electron density of the LUMO for **1** is localized on both the phenyl and TZD rings. Due to this, its ICT character is weaker than that of **8**. It should be noted that the electron density of the LUMO orbital for **12** is dominantly populated on the phenyl ring due to strong electron accepting character of the nitro substituent causing π -electron density shift to arylidene moiety regardless of oppositely oriented, but weaker effects of the TZD moiety.

Obviously, the ICT process is more feasible in compounds **8** and **12**. For compound **8**, the reason is higher planarity, while, in compound **12**, higher rotation around the bond connecting the electron donor and acceptor group can decouple the orbitals of these two groups providing means by which nearly complete charge transfer from the donor to the acceptor can occur. The highly polarizable



Fig. 6. The molecular orbitals and energy gaps between HOMOs and LUMOs of compounds 1, 8 and 12.

twisted excited state of compound **12** can be, under appropriate solvent conditions, preferentially stabilized with respect to the ground state (Table 3). Due to this, the excited and ground states are closer and more rapid internal conversion is permitted. Variation of substituent patterns clearly indicates that contributions of both twist and donor–acceptor character are involved in the ICT mechanism of the investigated molecules.

4. Conclusions

Solvent effects on the absorption maxima shifts of the investigated compounds were successfully evaluated by using the Catalán solvent parameter set. Solvent polarizability is the principal factor which influences the shift of absorption maxima, whereas the solvent dipolarity, acidity and basicity are less important. The absorption maxima undergo a bathochromic shift with increasing solvent polarizability indicating that the excitation state is more polarizable than the ground state. Specific interactions through hydrogen bonding, expressed by solvent acidity and basicity, can be attributed mainly to the carbonyl moiety and NH hydrogen and they are only slightly affected by the arylidene substituent. Moreover, different substituents significantly change the extent of conjugation in the molecules and further affect their ICT character. The correlation results imply that the solvatochromic properties are the consequence of the overall effect of the molecule geometry influenced by the electronic substituent effects transmitted through π -conjugated systems. The results obtained in this study help in assessing the potential application of the investigated compounds in different homogeneous media.

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